

TITLE: NOVEL SUPPORTED BIMETALLIC CARBIDE
CATALYSTS FOR COPROCESSING OF COAL WITH WASTE
MATERIALS

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ABSTRACT

OBJECTIVE

The overall objectives of this project are to explore the potential of novel supported bimetallic carbide catalysts for coal/waste coprocessing, and to understand the fundamental chemistry related to the reaction pathways of coprocessing and the role of the catalysts in the conversion of coal/waste into liquid fuels. The catalysts to be tested include unsupported and supported monometallic and bimetallic carbides based on molybdenum and niobium.

ACCOMPLISHMENTS TO DATE

A new family of bimetallic oxycarbide compounds $M^I-M^{II}-O-C$ ($M^I = Mo, W$; $M^{II} = V, Nb, Cr, Fe, Co, Ni$) has been synthesized by carburizing bimetallic oxide precursors using a temperature-programmed method. The catalysts were characterized by CO chemisorption, BET surface area measurement, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and near-edge X-ray absorption fine

structure (NEXAFS). The NEXAFS spectra of the carbide catalysts indicate that surface contamination by oxygen and the presence of an oxycarbide instead of a pure carbide structure.

The unsupported monometallic (Mo_2C) and bimetallic ($\text{NbMo}_{1.6}\text{C}$) catalysts were examined in a simulated coprocessing by model tests using a single compound (4-(1-naphthylmethyl)bibenzyl, abbreviated as NMBB) and five model compounds (NMBB, pyrene, dibenzothiophene, abbreviated as DBT, quinoline and eicosane) simultaneously at 375 °C and 400°C.

As we have indicated in the previous abstract, NMBB is a good model compound for examining activities and selectivities of various catalysts for C-C bond cleavage and hydrogenation, since there are different types of potential cleavage sites of C-C bonds and both monocyclic and bicyclic aromatic moieties in the compound. In addition, some other MoS_2 based laboratory-prepared and commercial catalysts have been examined for comparison.

The results from single NMBB compound and 5-component reactions showed that $\text{NbMo}_{1.6}\text{C}$ catalyst showed higher activities than Mo_2C catalyst in terms of hydrogenation, hydrocracking, hydrodesulfurization and hydrodenitrogenation based on the same active sites charged. $\text{NbMo}_{1.6}\text{C}$ has very high activity for hydrogenation of bibenzyl derivatives, as well as naphthalene. Compared to other MoS_2 based catalysts, Mo_2C and $\text{NbMo}_{1.6}\text{C}$ carbide catalysts showed different catalytic functionalities on NMBB. More deep hydrogenated products such as decalin and hydrogenated products of 4-methylbibenzyl have been found when the reaction was catalyzed by $\text{NbMo}_{1.6}\text{C}$. The experiments with 5-component mixture showed that the patterns of product distributions strongly depend on the type of catalysts, and the trends do not always parallel with those for single-component tests, indicating the influence of co-reactants.

The reaction temperature also showed large effect on the product distribution. More hydrogenation products and very limited C-C cleavage products were achieved at 375°C, while higher yields of hydrocracking, and hydrogenated C-C cleavage products were detected at 400°C. Meanwhile, two commercial catalysts, CR-344 (Co-Mo/ Al_2O_3) and CR-424 (Ni-Mo/ Al_2O_3) and dispersed MoS_2 catalyst derived in-situ from ammonium tetrathiomolybdate [ATTM, $(\text{NH}_4)_2\text{MoS}_4$] were investigated under the same conditions. Ni-Mo/ Al_2O_3 shows higher hydrogenation activity than Co-Mo/ Al_2O_3 .

FUTURE WORK

We will continue the study of the new catalysts. We are attempting reaction with both plastic and rubber reactions. In addition, we are investigating the radical reaction chemistry in catalytic coprocessing using ^{13}C NMR.

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STUDENTS SUPPORTED UNDER THIS GRANT

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